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Study of elastic constants and bulk modulus of alkaline earth solids under the effect of high temperature

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Abstract A simple theoretical method is proposed to predict the second-order elastic constants and bulk modulus of fluoride crystals as a function of temperature. The potential free model based on the thermo-dynamical relations has been employed for the calculation work. It is found that the calculated values of the elastic constants, in general, decrease with temperature. The theoretical prediction as reported in the present paper for CaF_2, SrF_2, BaF_2 and PbF_2 crystals are well supported by the available experimental data. However, in case of PbF_2, the theoretical results particularly above 800 K could not be compared with experimental values as the experimental data above 800 K is not available.

Keywords Alkaline earth solids, elastic constants, high temperature

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1. Introduction

The temperature-dependent properties of various classes of solids are of fundamental interest to the geophysical and geochemical theories of earth interior [1,2]. For the temperature dependence of elastic properties, Gong *et al* [3] presented Monte Carlo and lattice dynamical studies using a rigid ion model. Singh *et al* [4] developed a three-body potential model for the temperature variation of elastic constants. They have calculated the temperature dependence of elastic constants for CaF_2, SrF_2, BaF_2 and PbF_2 crystals. The results achieved by them are claimed to be close to the experimental data. However, there are some weaknesses in the model adopted by them. These are (i) the short-range overlap potential parameters calculated by them at 300 K have been considered as the invariant parameters with temperature and used as such values even in high temperature range, (ii) the Van der Waals coefficient calculated from the lattice sums have also been considered temperature independent. Vandana *et al* [5] have recently calculated the interionic separation (r) for various minerals and crystals and noted that r varies with temperature. It is therefore desirable that the short-range overlap and Van der Waals interaction parameters should be considered as a function of temperature and thus the approach followed by these workers is not physically realistic.

To overcome these difficulties, we have employed a potential free model which is based only on thermo-dynamical relations. The main purpose of the present study is to provide a straightforward and simple method, rather than a potential model based on several approximations, to explain the temperature-dependent properties of solids. In the present paper we have estimated the temperature dependence of second order elastic constants (SOEC) and bulk modulus of CaF_2, SrF_2, BaF_2 and PbF_2 crystals starting from room temperature to melting temperature. The method of the present analysis is given in Section 2. Results are discussed and compared with the experimental data in Section 3.

2. Method of analysis

The expressions for second order elastic constants (SOEC) have been reported by Wallace [6] to study cubic crystals under isotropic pressure [7].

$$C_{11} = C^0_{11} - P_{\text{phonon}}, \quad (1)$$

$$C_{12} = C^0_{12} - P_{\text{phonon}}, \quad (2)$$

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and $C_{44} = C^{o}_{14} - P_{phonon}$, (3)

where C_{ij} represent the SOEC at temperature T, and Co_{ij} are their values at $T = T_0 = 300$ K; P_{Phonon} is the phonon pressure or thermal pressure (P_{Th}). The thermal pressure may be evaluated in the traditional way [8-10].

$$\frac{\partial p}{\partial T} \qquad \frac{\partial p_{Th}}{\partial T} \Big| = \alpha_0 B_T^0 \tag{4}$$

On integration of eq. (4), we get

$$P_{Th} = \int_{T_0}^{T} \alpha_0 B_T^0 \, dT \tag{5}$$

or $$P_{Th} = \alpha_0 B_T^0 (T - T_0), \tag{6}$$

where α_0 and B_T^0 are the coefficient of volume thermal expansion and bulk modulus respectively and **0** refers to their values at $T = T_0$.

The Anderson-Gruneise parameters is defined as follows :

$$\delta_T = -\frac{V}{B_T}\left[\frac{dB_T}{dV}\right]_t \tag{7}$$

or $$\frac{dB_T}{B_T} = -\delta_T \frac{dV}{V}, \tag{8}$$

where V is the volume.

On integrating eq. (8) at constant pressure and assuming δ_T to be constant, *i.e.*

$$\int_{B_T}^{B_t} \frac{dB_T}{B_T} = -\delta_T \int_{V_0}^{V} \frac{dV}{V} \tag{9}$$

one can get $B_T / B_T^0 = \left(V\right)^{-\delta_t}$ (10)

The empirical temperature independence of δ_T and αB_T^0 is assumed as in case of minerals [1]. The Anderson parameter δ_T can also be defined as [8]

$$\delta_T = -\frac{1}{\alpha B_T}\left(\frac{dB_T}{dT}\right)_P \tag{11}$$

On integrating eq. (11), *i.e.*

$$\int_{B_0}^{B_T} dB_T = -(\alpha_0 B_0 \delta_0) \int_{T_0}^{T} dT,$$

the following equation for the bulk modulus is obtained as a function of temperature.

$$B_T = B_T^0\left[1 - \alpha_0 \delta_0 (T - T_0)\right]. \tag{12}$$

The value of B_T as a function of temperature can thus be calculated for eq. (12). Thus on generalizing eq. (10), one can get

$$\frac{M}{M_0} \qquad V^{-\delta_{ij}^0} \tag{13}$$

when M represents any of the second order elastic moduli such as C_{11}, C_{12} and C_{44}. On the basis of eq. (13), the relevant expressions for C_{11}, C_{12} and C_{44} can thus be written collectively as follows :

$$\frac{C_{ij}}{C_{ij}^0} = \left(V\right)^{-\delta_{ij}^0} \tag{14}$$

where δ_{ij}^0 are constant corresponding to C_{ij}^0 and are defined as follows :

$$\delta_{ij}^0 = -\frac{1}{\alpha_0 C_{ij}^0}\frac{dC_{ij}}{dT} \tag{15}$$

In previous studies [11, 12], the calculations have been made to analyse the thermal expansion and elastic properties of minerals and crystals by using one of the eqs. (12-15) They have claimed their results close to available experimental data However, the main drawback in previous studies has been noted that the Anderson-Gruneise parameter δ_T considered by them to be a constant parameter throughout their calculation Since the expressions of elastic constants and bulk modulus are represented in terms of δ_T which is also the temperature-dependent parameter, these expressions should have been considered as a function of temperature separately. Motivated with this situation, we have therefore assumed the Anderson parameter (δ_T) to be a function of temperature in the present study. We have assumed

$$\delta_{ij} = \delta_{ij}^0 \Big| \frac{T}{T_0} \tag{16}$$

where $k = 0.25$, a best fitting value for fluoride crystals

In the present study, we have first calculated the different values of δ_{ij} above the room temperature for each of the fluoride crystal and then used them in eqs. (12-14) to predict the values of C_{11}, C_{12} and C_{44} and bulk modulus at higher temperature The calculated values of δ_{ij} above the room temperature are given in Table 2. The value of bulk modulus and three elastic constants predicted for four alkaline earth fluoride crystals are shown in Tables (3a-3d). The available experimental data are also shown along with the calculated results for the sake of comparison. The input data at room temperature are reported in Table 1 [15-17].

Table 1. Data of input parameters at room temperature [Refs 15-17] value for the following crystals.

Parameter	CaF_2	SrF_2	BaF_2	PbF_2
α_0 (10^{-5} K^{-1})	5.565	5.46	5 49	7.146
	4.6	4 82	4 71	4.66
B_T^0 (10^{10}N/m^2)	8.23	7.129	5.882	6.292
C_{11}^0 (10^{10} N/m^2)	16 55	12 461	9.244	9 637
C_{12}^0 (10^{10} N/m^2)	4.07	4.463	4.212	4.663
C_{44}^0 (10^{10} N/m^2)	3.35	3.187	2.536	2 104
$(dC_{11}/dT)_0$, 10^7N/m^2	−3.185	−2.39	−2.04	−3.36
$(dC_{12}/dT)_0$, 10^7N/m^2	−1.05	−1 24	−1 305	−2.00
$(dC_{44}/dT)_0$, 10^7N/m^2	−1.22	−0 92	−0.734	−0 78

Table 2. Calculated values of Anderson parameters δ_i (in dimensionless units) from eq (16) [17]

Temperature (K)	CaF_2	SrF_2	BaF_2	PbF_2
300	4.62	4.82	4 71	4 66
400	4 964	5.179	5 061	5 008
500	5.249	5.477	5.351	5 295
600	5 494	5 732	5 601	5 412
700	5 709	5 957	5.821	5 759
800	5 904	6.159	6.019	5 955
900	6 08	6 343	6.199	6.133
1000	6 242	6 573	6 364	6 297
1100	6 393	6 669	6.517	6 448
1200	6 534	6 816	6.661	6 59

Table 3a. Calculated and experimental (in parenthesis) values of elastic constants and bulk modulus (× 10^{10} N/m^2) of CaF_2 crystal [Refs. 12, 13].

Temperature (K)	C_{11}		C_{44}	B_T
300	16.55 (16.55)	4 07 (4 07)	3 35 (3 35)	8 230
400	16.23 (16 26)	3.966 (3.929)	3.23 (3.266)	8 001
500	15 90 (16.06)	3.858 (3 859)	3.106 (3.200)	7 737
600	15.58 (15.80)	3.753 (3.824)	2.987 (3.13)	7 464
700	15.25 (15.46)	3.648 (3 754)	2.870 (3.066)	7.178
800	14.99 (15.00)	3.534 (3.684)	2.745 (3.00)	6.858
900	14 543 (14.66)	3.422 (3 578)	2.623 (2.866)	6.535
1000	14.178 (14.20)	3.308 (3.438)	2.499 (2 700)	6.199
1100	13 801 (13.80)	3.190 (3.298)	2.375 (2.600)	5 855
1200	13.409 (13.20)	3.069 (3.228)	2.249 (2.53)	5.498

Table 3b. Calculated and experimental (in parenthesis) values of elastic constants and bulk modulus (× 10^{10} N/m^2) of SrF_2 crystal [Refs 13, 14]

Temperature (K)			C_{44}	B_T
300	12 46 (12.46)	4 463 (4 463)	3.187 (3 187)	7.129
400	12 223	4.340	3 096	6.929
500	11 978 (11 893)	4 214 (4 415)	3.003 (3 117)	6 703
600	11 731	4 089	2.910	6 460
700	11.478 (11 434)	3.962 (3 929)	2 816 (2 946)	6 202
800	11 219	3 833	2.721	5 930
900	10 953 (10 792)	3 702 (3 708)	2 625 (2 716)	5.648
1000	10 678 (10 625)	3 569 (3 634)	2 526 (2 617)	5 355
1100	10 394 (10 358)	3 432	2 426	5 052
1200	10 098 (9 975)	3 292 (3 438)	3 323 (2 455)	4 741

Table 3c. Calculated and experimental (in parenthesis) values of elastic constants and bulk modulus (× 10^{10} N/m^2) of BaF_2 crystal [Refs 13, 14].

Temperature (K)		C_{12}	C_{44}	
300	9.244 (9 244)	4 212 (4 212)	2 536 (2 536)	5 882 (5 882)
400	9.067 (9 076)	4 099 (4 107)	2 473 (2 497)	5 741 (5 747)
500	8 892 (8 805)	3 989 (3 916)	2 410 (2 455)	5.586 (5 555)
600	8 714 (8 518)	3 877 (3 723)	2.347 (2 378)	5 417 (5 319)
700	8 530 (8 239)	3 763 (3.538)	2 282 (2.292)	5.236 (5.102)
800	8 347 (7 958)	3 649 (3.369)	2 218 (2 202)	5 048 (4.901)
900	8 159 (7 682)	3 534 (3 216)	2 153 (2 119)	4 851 (4 694)
1000	7 968 (7 358)	3 418 (3 040)	2.087 (2 026)	4 648 (4.482)
1100	7 769 (6 785)	3 299 (2.674)	2 019 (1 924)	4.437 (4.048)
1200	7 566 (5 865)	3.9215 (2 157)	1.950 (1 802)	4 220 (3.389)

3. Results and discussion

We have proposed a very simple method for the determination of temperature-dependence of elastic constants and bulk modulus. There results of temperature-dependence of elastic constants calculated from eq. (14) in view of eq. (16) are reported in Tables 3a-3d. We have also used a similar simple relationship

Table 3d. Calculated and experimental (in parenthesis) values of elastic constants and bulk modulus ($\times 10^{10}$ N/m^2) of PbF_2 crystal [Refs. 13, 14].

Temperature (K)			C_{44}	B_v
300	9 637	4.663	2.104	6.292
	(9 637)	(4 663)	(2 104)	(6.292)
400	9 301	4.464	2 026	6.067
	(9 034)	(4.464)	(2 065)	(5.845)
500	8.963	4.265	1 948	5 816
	(8 441)	(4 266)	(2.013)	(5 371)
600	8.621	4.064	1 869	5.544
	(7 764)	(4 071)	(1 881)	(4 975)
700	8 276	3.866	1 789	5.544
	(6 545)	(3 878)	(1 783)	(4 975)
800	7 922	3.664	1.708	4 953
	(4 384)	(3 688)	(1 511)	(2 903)
900	7 560	3.459	1 626	4 964
1000	7 189	3.252	1 541	4 482
1100	6.805	3 039	1 453	4 048
1200	6 406	2 822	1.364	3 389

given by Wallace [6] and advocated by Shrivastava [7]. It can be noted from Tables (3a-3d) the results achieved in the present work are in good agreement with the available experimental data [13, 14] for all four crystals for each elastic constant. The trend of decrement of the elastic constants with temperature is also found in agreement with the experimental data [13].

The simple method developed in the present work is thus free from the theory of potentials and the results obtained are in good agreement with the complete simulation studies as well. The variation of C_{11} with temperature is found to be large but for C_{12} small and for C_{14} smaller. The constant C_{11} represents elasticity in length. A longitudinal strain produces a change in volume without a change in shape. The volume change is closely related to the temperature and thus produces a large change in C_{11}. On the other hand, the constants C_{12} and C_{44} are related to the elasticity in shape without a change in volume. Thus, C_{12} and C_{44} are less sensitive to temperature. On the basis of overall descriptions, it may thus be concluded that the model theory used here is not only simple but also superior to the earlier potential models based on several approximations. The approach is independent of crystal structure and may be extended to the more complex solids of geophysical importance and application.

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